

PATENT SPECIFICATION

NO DRAWINGS

958.924

958.924



Date of Application and filing Complete Specification: Nov. 9, 1962.

No. 42503/62.

Application made in Switzerland (No. 13477) on Nov. 20, 1961.

Complete Specification Published: May 27, 1964.

© Crown Copyright 1964.

RECEIVED

DEC 28 2004

IPO
GENERAL ELECTRIC CO.

Index at acceptance:—C4 P (Q2E, Q4A3, Q4A8)

International Classification:—C 09 b

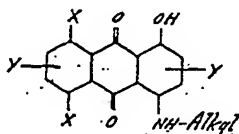
COMPLETE SPECIFICATION

Alkylated Dihydroxy-Diaminoanthraquinones and process for their manufacture

We, CIBA LIMITED, a body corporate organised according to the laws of Switzerland, of Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention provides alkylated dihydroxy-diaminoanthraquinones of the formula

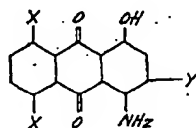
1)



in which one X represents a hydroxyl group and the other X represents an amino group, one Y represents an alkyl group that may be substituted and the other Y a hydrogen atom.

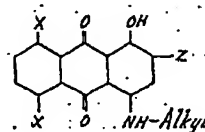
The dyestuffs of the invention are obtained by treating a dihydroxy-diaminoanthraquinone of the formula

2)



20 with alkylating agents, or by condensing the leuco compound of a dihydroxy-diaminoanthraquinone of the formula

3)



with an aldehyde in the presence of a hydro-sulphite. In the above formulae one X represents a hydroxyl group and the other X an amino group, Y represents an alkyl group that may be substituted and Z represents a hydrogen atom or a sulphonic acid group.

The starting materials of the formula 2) contain as alkyl residues advantageously lower alkyl residues, for example, methyl, ethyl, propyl, isopropyl or butyl residues or substituted alkyl residues, such, for example, as benzyl or furfuryl groups. As examples there may be mentioned the following compounds:

- 1:5 - dihydroxy - 4:8 - diamino - 3 - methyl-anthraquinone,
- 1:5 - dihydroxy - 4:8 - diamino - 3 - ethyl-anthraquinone,
- 1:5 - dihydroxy - 4:8 - diamino - 3 - pentyl-anthraquinone,
- 1:5 - dihydroxy - 4:8 - diamino - 3 - benzyl-anthraquinone,
- 1:5 - dihydroxy - 4:8 - diamino - 3 - furfuryl-anthraquinone, and
- 1:8-dihydroxy - 4:5 - diamino - 3 - methyl-anthraquinone.

Mixtures of the aforesaid compounds can be used as well as the homogeneous compounds.

Such compounds can be obtained by a

[Price 4s. 6d.]

Price 33p

Price 33p

known method by reacting leuco-1:5-dihydroxy-4:8-diamino- or 1:8-dihydroxy-4:5-diamino-anthraquinone or the corresponding sulphonic acids with aldehydes, for example; formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, benzaldehyde or furfural. As alkylating agents there may be used alkyl-halides, such, for example, as methyl chloride, methyl bromide, ethyl bromide or benzyl chloride, aryl sulphonic acid alkyl esters as, for example, benzene- or para-toluene-sulphonic acid methyl ester or ethyl ester, and, more especially, sulphuric acid alkyl esters such, for example, as dimethyl sulphate or diethyl sulphate. Instead of the dialkyl sulphates there can be used with the same success a mixture of an aliphatic alcohol, especially methanol, ethanol or propanol and sulphuric acid. The operation is advantageously carried out at a raised temperature, especially within the range of 100 to 150°C. The alkylation is advantageously carried out in a solvent, for example, in nitrobenzene, chlorobenzene or sulphuric acid. Instead of a solvent, a large excess of the alkylating agent can also advantageously be used.

Under the aforesaid alkylating conditions generally only one alkyl group is introduced into an amino group.

The starting materials of the formula (3) contain as alkyl residues advantageously lower alkyl residues, for example, methyl, ethyl, propyl, isopropyl residues or substituted alkyl residues, such, for example, as benzyl residues. They are obtained by treating 1:5-dihydroxy-4:8-diamino- or 1:8-dihydroxy-4:5-diamino-anthraquinone with alkylating agents. As examples there may be mentioned the following:

- 1:5 - dihydroxy - 4 - amino - 8 - methyl-amino-anthraquinone,
- 1:5 - dihydroxy - 4 - amino - 8 - ethyl-amino-anthraquinone,
- 1:5 - dihydroxy - 4 - amino - 8 - isopropyl-amino-anthraquinone,
- 1:5 - dihydroxy - 4 - amino - 8 - methyl-amino-anthraquinone-2-sulphonic acid; and
- 1:8 - dihydroxy - 4 - amino - 5 - methyl-amino-anthraquinone-2-sulphonic acid,

the last two of which may be prepared by methylating 1:5-dihydroxy-4:8-diamino- or 1:8 - dihydroxy - 4:5 - diaminoanthraquinone-2-sulphonic acid.

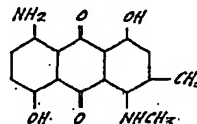
The new compounds obtained by the process of the invention are valuable dyestuffs. They can be used singly or in admixture with one another, advantageously after conversion into a dispersion, for dyeing hydrophobic fibres, advantageously those made from aromatic polyesters, such, for example, as polyethylene terephthalates, on which they display a good build-up. They yield pure blue dyeings possessing a good fastness to light and a good fastness to sublimation.

The following Examples illustrate the inven-

tion. Unless otherwise stated, the parts and percentages are by weight.

EXAMPLE 1

28.4 Parts of 1:5-dihydroxy-4:8-diamino-3-methylanthraquinone are dissolved and introduced into 150 parts of sulphuric acid of 98% strength. 32 Parts of methanol are added while cooling, and the whole is then heated for 3 hours at 130 to 135°C. When cold, the reaction products is poured on to ice and the dyestuff precipitates. The dyestuff is then isolated by suction filtration and washed with water. The dry dyestuff, which probably has the formula



is a blue powder. The yield amounts to 80 to 90%.

When applied to polyester from an aqueous dispersion the dyestuff so obtained yields greenish blue dyeings possessing a good fastness to light.

If in the above alkylation process ethanol or propanol is used instead of methanol, dyestuffs are obtained which yield on polyester fibres dyeings having similar properties.

EXAMPLE 2

37.2 Parts of the sodium salts of 1:5-dihydroxy - 4:8 - diamino - anthraquinone - 2-sulphonic acid are dissolved in 400 parts of concentrated sulphuric acid. 32 Parts of methanol are then added to the solution while cooling, and the whole is heated for 3 hours at 130 to 135°C. The cold reaction mixture is poured on to ice and the product is isolated. The sodium salt of 1:5-dihydroxy-4-methylamino-8-aminoanthraquinone-2-sulphonic acid can be obtained by a treatment with caustic soda solution or sodium carbonate and salting out.

35 Parts of the resulting 1:5-dihydroxy-4-methylamino - 8 amino - anthraquinone - 2-sulphonic acid are dissolved in 1500 parts of water, and the solution treated with 10 parts of an aqueous formaldehyde solution of 40% strength. After that, 36 parts of sodium hydrosulphite are added and the whole stirred for one hour at 90-95°C. By adding 200 parts of sodium hydroxide solution of 30% strength and introducing a current of air, the 1:5 - dihydroxy - 4 - methylamino - 8-amino - methylanthraquinone is precipitated and then isolated by filtration. The resulting dyestuff has the same properties as the one obtained according to the first paragraph of Example 1.

When in the procedure described in the preceding paragraph, formaldehyde is replaced by acetaldehyde, propionic aldehyde or benzaldehyde, dyestuffs having very similar properties are obtained.

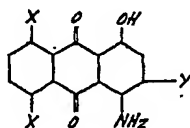
EXAMPLE 3

1 Part of an aqueous paste of the dyestuff obtained in the manner described in Example 1 and approximately 1 part of dried sulphite cellulose waste liquor are ground in a roller mill to form a fine paste with a dyestuff content of about 10%.

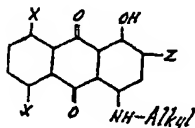
100 Parts of fibrous material of polyethylene-terephthalate are washed for 30 minutes in a bath containing, per 1000 parts of water, 1 to 2 parts of the sodium salt of N-benzyl- μ -heptadecyl-benzimidazole-disulphonic acid and 1 part of a concentrated aqueous ammonia solution. The material is then entered into a dyebath of 3000 parts of water in which 10 parts of the dyestuff paste obtained in the manner described in the first paragraph have been dispersed in the presence of 4 parts of the sodium salt of N-benzyl- μ -heptadecyl-benzimidazole-sulphonic acid. The whole is then heated to 120°C in a pressure vessel and maintained at that temperature for $\frac{1}{2}$ hour. The material is then well rinsed, and, if necessary, washed for $\frac{1}{2}$ hour at 60 to 80°C with a solution containing, per 1000 parts of water, one part of the sodium salt of N-benzyl- μ -heptadecylbenzimidazole-disulphonic acid. There is obtained a greenish blue dyeing possessing a good fastness to sublimation and a good fastness to light.

WHAT WE CLAIM IS:—

1. A process for the manufacture of alkylated dihydroxy-diaminoanthraquinones, wherein a dihydroxy-diaminoanthraquinone of the formula.



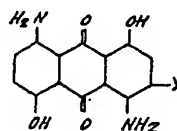
or a mixture of the aforesaid compounds is treated with an alkylating agent, or the leuco compound of a dihydroxy-diaminoanthraquinone of the formula



is condensed with an aldehyde in the presence of a hydrosulphite, in which one X in the above formulae represents a hydroxyl group and the other X represents an amino group,

Y represents an alkyl group that may be substituted, and Z represents a hydrogen atom or a sulphonic acid group.

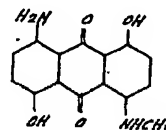
2. A process as claimed in claim 1, wherein a dihydroxy-diaminoanthraquinone of the



formula

or a mixture of compounds of this formula in which Y represents an alkyl group, is treated with an alkylating agent.

3. A process as claimed in claim 1, wherein the leuco compound of the anthraquinone of the formula



is condensed with an aldehyde in the presence of a hydrosulphite.

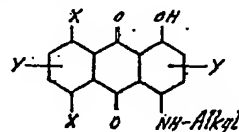
4. A process as claimed in claim 3, wherein the aldehyde used is formaldehyde.

5. A process as claimed in claim 2, wherein a mixture of an aliphatic alcohol and sulphuric acid is used as alkylating agent.

6. A process as claimed in claim 1, conducted substantially as described in Example 1 or 2 herein.

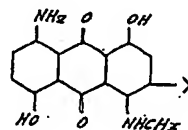
7. Alkylated dihydroxy-diaminoanthraquinones, whenever obtained by the process claimed in any one of claims 1 to 6.

8. Alkylated dihydroxy-diaminoanthraquinones of the formula



in which one X represents a hydroxyl group and the other X represents an amino group, one Y represents an alkyl group that may be substituted and the other Y represents a hydrogen atom.

9. Dihydroxy-diaminoanthraquinones of the formula



in which Y represents an alkyl residue that may be substituted.

10. Any one of the alkylated dihydroxy-diaminoanthraquinones as claimed in claim 7 and which is described in any one of the Examples herein.
- 5 11. A process for dyeing or printing polyester fibres, wherein there are used the dye-stuffs as claimed in any one of claims 7 to 10 or mixtures thereof.
12. A process for dyeing polyester fibres conducted substantially as described in 10 Example 3 herein.
13. Polyester fibres dyed or printed by the process claimed in claim 11 or 12.

ABEL & IMRAY,
Chartered Patent Agents,
Quality House, Quality Court,
Chancery Lane,
London, W.C.2.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press (Leamington) Ltd.—1964. Published by The Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.